(54) ISOPARAFFIN-OLEFIN ALKYLATION

(71) We, MOBIL OIL CORPORATION, a Corporation organised under the laws of the State of New York, United States of America, of 150 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention pertains to a process for alkylation by reaction of an isoparaffin and an olefin.

Alkylation achieved as a result of reaction between an isoparaffin and an olefin has heretofore been recognized as resulting in an alkylate product useful as a high octane blending stock in gasoline.

Sulfuric acid and HF alkylation processes have been used for the production of such alkylate. These processes employ liquid-liquid catalytic systems which are known to be expensive and troublesome because of such problems as maintaining an acid/hydrocarbon emulsion, product separation and waste disposal.

In order to overcome such problems, attempts have been made in the past to conduct the desired alkylation in a heterogeneous catalyst system. One such attempt described in U.S. 3,251,902 has involved the use of crystalline aluminosilicate zeolites as catalysts. While certain of such crystalline aluminosilicate zeolites have been found to be effective catalysts for isoparaffin/olefin alkylation, they have the disadvantage of aging rapidly and requiring frequent regeneration to maintain requisite selectivity.

Another approach which has been suggested in the past is the use of a catalyst for effecting the desired isoparaffin/olefin alkylation of a complex of a microreticular or gel type ion exchange resin and boron trifluoride. The use of such complex, although suggested almost twenty years ago, see for example U.S. 2,843,642, has not been adopted on a commercial scale due to side formation of unwanted olefinic products and relatively low selectivity for the desired branched alkylate product. Moreover, in view of their lack of commercial appeal little or no attention has been devoted to regeneration of such catalysts.

According to the present invention a process for alkylating an isoparaffin having from 4 to 8 carbon atoms comprises contacting the same in the liquid state at a temperature between −20°C and 150°C, with a catalyst comprising a cation exchange resin containing acid groups and boron trifluoride, the molar ratio of said isoparaffin to said olefin being between 2 and 50, said resin being a macroreticular acid cation exchange resin having a water content between 0.5 and 20 weight percent and a surface acid concentration of less than 0.5 milliequivalents of hydrogen ion per square meter of surface area.

In the preferred embodiment the boron trifluoride is present in an amount in excess of that needed to saturate the resin: moreover, the contacting may be performed in the presence of 10 to 400 ppm. of water. However, in an alternative embodiment the resin contains a quantity of boron trifluoride between 0.1 eq. per equivalent of resin acid groups and the amount required for saturation of the resin, and also contains a quantity of hydrogen fluoride between 0.1 and 10 equivalents per equivalent of resin acid groups. The hydrogen fluoride, when employed, may be associated with the resin by virtue of having contacted it in admixture with the isoparaffin. In all embodiments the resin may be periodically regenerated by extraction with a polar solvent. The invention is advantageously put into practice in a continuous manner. Thus, in one desirable mode of operation the boron trifluoride is added to a mixture of the isoparaffin and the resin, the resulting admixture is stirred to promote effective contacting of its components, and the olefin is added to the stirred admixture. In another the isoparaffin, olefin and boron trifluoride are

continuously charged to the resin, the resulting admixture is continuously stirred to promote alkylation, and hydrocarbon mixture containing alkylate is continuously withdrawn from said stirred admixture.

The process is preferably carried out at a temperature between −20°C. and 60°C. The surface acid concentration of the resin is preferably between 0.001 and 0.2 milliequivalents of hydrogen ion per square meter of surface area, and the preferred resin is a macroreticular sulfonic acid cation exchange resin such as sulfonated styrene-divinylbenzene copolymer. Resin surface area is advantageously between 30 and 800 m^2/g. When the BF_3 is employed in excess of that needed to saturate the resin the equivalent ratio of BF_3 of resin acid groups desirably exceeds 2.

A particularly interesting application of the process of the invention is that in which the olefin contains 4 carbon atoms and the isoparaffin is isobutane: the preferred molar ratio of isoparaffin to olefin is, generally, between 3 and 10.

When the contacting is performed in the presence of water the amount of water is preferably 10 to 300 ppm, still more preferably 20 to 200 ppm. The water, however, need not be present as such but may be employed in the form of a water-forming material, typically methanol or tertiarybutyl alcohol.

The polar solvent employed in regeneration is preferably water or an alcohol, alcohols having from 1 to 5 carbon atoms, particularly methanol, being preferred.

The invention will be described in conjunction with the accompanying drawings in which:

Fig. 1 depicts relationship between selectivity and resin surface acid concentration.

Figs. 2 and 3 illustrate continuous modes of operation.

Fig. 4 illustrates a process scheme which incorporates provision for catalyst regeneration.

Fig. 5 illustrates a semi-continuous mode of operation.

Fig. 6 depicts the relationship between yield of alkylate and catalyst age in a continuous and semi-continuous process.

Fig. 7 depicts the relationship between quality of alkylate and catalyst age in a continuous and semi-continuous process.

Fig. 8 depicts relationship between selectivity and surface area of resin.

Fig. 9 depicts relationship between octane number and surface area of resin.

Fig. 10 depicts relationship between selectivity and temperature.

Fig. 11 depicts relationship between octane number and temperature.

Fig. 12 depicts the relationship between yield of alkylate and time on stream in the presence of varying amounts of water equivalent.

Fig. 13 depicts the relationship between quality of alkylate and time on stream in the presence of varying amounts of water equivalent.

Fig. 14 depicts relationship between yield of alkylate and time on stream in the presence of small amounts of water introduced from different alcohols.

Fig. 15 depicts relationship between quality of alkylate and time on stream in the presence of small amounts of water introduced from different alcohols.

Fig. 16 depicts the alkylate yield performance of fresh and regenerated catalyst.

Fig. 17 depicts the alkylate quality achieved with fresh and regenerated catalyst.

In accordance with the present invention, there is provided an isoparaffin/olefin alkylation process which overcomes many of the disadvantages of those previously employed and/or suggested. The method described herein, in contrast to that of U.S. 2,843,642, utilizes a catalyst which is a complex of a macroreticular as opposed to microreticular acid cation exchange resin and boron trifluoride. Moreover, a particular class of macroreticular acid cation exchange resin is employed which class is characterized by substantial porosity, high surface area and a low surface acid concentration, generally less than 0.5 milliequivalents of hydrogen ion per square meter surface area. For effecting the desired alkylation, the cation exchange resin should contain between 0.5 and 20 percent by weight of water. The use of such catalyst has been found, unexpectedly, to result in an attractive yield of alkylate product of high octane number.

The macroreticular resins utilized in the process of this invention are characterized by the presence of acid funcitonal groups and a structure having a high degree of trueporosity while possessing rigidity and being subject to minimum volume change when immersed in or removed from solvents or solutions.

A macroreticular acid ion exchange resin employed according to the invention is typified by the presence of sulfonic acid groups, e.g. the sulfonated styrene-divinylbenzene copolymer exchange resins such as those commercially available as Amberlyst-15, Amberlyst XN-1005, Amberlyst XN-1010, Amberlyst XN-1011, Amberlyst XN−1008 and Amberlite 200. The properties of these resins, along with Amberlite IR-120H, a typical microreticular resin, and Amberlite XAD-4, a styrene-divinylbenzene polymer with no ion exchange capacity, are shown below ("Amberlyst" and "Amberlite" are Registered Trade Marks).

	Macroreticular			
	Amberlyst-15	Amberlyst-XN-1005	Amberlyst XN-1010	Amberlyst XN-1011
Skeletal Structure	Styrene-DVB	Styrene-DVB	Styrene-DVB	Styrene-DVB
Ionic Functionality	RSO_3H	RSO_3H	RSO_3H	RSO_3H
Hydrogen Ion Concentration meq/g dry (Exchange Capacity)	4.9	3.4	3.3	4.2
Porosity, %	32	42	47	24
Avg. Pore Diameter, A°	200-600	80-90	40-50	—
Cross-linkage	20	—	—	—
Surface Area, M^2/g dry	40-50	100-120	550-600	28
Surface Acid Concentration neq H^+/m^2 S.A.	0.102	0.031	0.006	0.150

	Macroreticular			Microreticular
	Amberlyst-XN-1008	Amberlite-200	Amberlite-XAD-4	Amberlite-IR-120H
Skeletal Structure	Styrene-DVB	Styrene-DVB	Styrene-DVB	Styrene-DVB
Ionic Functionality	RSO_3H	RSO_3H	None	RSO_3H
Hydrogen Ion Concentration meq/g dry (Exchange Capacity)	4.5	4.3	0	5.0
Porosity, %	—	—	52	1.8
Avg. Pore Diameter, A°	400-800	—	50	—
Cross-linkage	—	20	—	8
Surface Area, M^2/g dry	30-40	40-50	750	<0.1
Surface Acid Concentration meq H^+/m^2 S.A.	0.129	0.096	0	>50

Surface acid concentration is determined by dividing the exchange capacity by the surface area in the dry state and is reported as milliequivalents of hydrogen ion per square meter surface area. The lower the surface acid concentration of the resin, the more effective is the resin/BF_3 catalyst for alkylation. The relationship between surface acid concentration of the resin in a resin/BF_3 catalyst and selectivity as determined as the weight percent of trimethylpentane in the C_5+ fraction for isobutane/butene-2 alkylation has been observed and is shown graphically in Fig. 1, from which it will be evident that the selectivity increases with decreasing resin surface acid concentration. The surface acid concentration of the resin should be below 0.5 milliequivalents of hydrogen ion per square meter surface area and preferably between 0.001 and about 0.2 milliequivalents of hydrogen ion per square meter surface area.

The described resin and BF_3 form a complex. Neither BF_3 alone nor the resin alone is an effective catalyst for the desired isoparaffin/olefin alkylation. Even the 1:1 complex (resin:BF_3) is relatively ineffective for alkylation, as is a resin-HF combination containing 2.7 equivalents of HF per equivalent of resin acid groups. It has been found desirable that the amount of boron trifluoride present be in excess of that required to saturate the resin. Thus, the most effective macroreticular resin/BF_3 alkylation catalysts have been found to be generally characterized by an equivalent ratio of BF_3/acid groups of resin exceeding two.

The catalyst and more particularly the cation exchange resin component thereof used in accomplishing the desired alkylation is characterized by a water content of between 0.5 and 20 weight percent and preferably between 1.5 and 15 weight percent. Cation exchange resins having a water content of less than 0.5 or greater than 20 weight percent were not found effective in achieving alkylation. Water can be introduced into the resin by contact with the requisite quantity of liquid water or by exposure to a moisture laden atmosphere for a time sufficient to introduce the desired water content. One suitable way of introducing requisite water to the resin is by equilibrating it with air at 100% relative humidity for a controlled period of time.

Alkylation using the described catalyst is carried out at a temperature below that at which the resin decomposes, i.e. generally below 150°C. A temperature as low as −20°C. or lower may be employed. Generally the temperature, under practical operating conditions, will be within the

approximate range of $-20°C.$ to $60°C.$ A particularly effective temperature range is from $-20°C.$ to $20°C.$

The pressure employed is sufficient to maintain the reactants in the liquid state. In general, the pressure will be between 50 and 1500 psig and preferably between 100 and 500 psig.

The isoparaffin reactant used in the present alkylation process is one having from 4 to 8 carbon atoms. Representative examples of such reactant are isobutane, 3 methylhexane, 2 methylbutane, 2,3—dimethylbutane and 2,4-dimethylhexane.

The olefin reactant employed contains from 2 to 12 carbon atoms. Representative examples are butene-2, isobutylene, butene-1, propylene, ethylene, hexene, octene and heptene. Particularly preferred is a C_4 olefin, i.e. butene-1, butene-2, or isobutylene either alone or in admixture.

The molar ratio of isoparaffin to olefin is generally between 2 and 50 and more particularly between 3 and 10. The weight ratio of resin to total hydrocarbon, that is isoparaffin, olefin and alkylate generally is between .01 and .5 and more particularly between 0.4 and .2.

The useful cycle life of the macroreticular acid cation exchange resin/boron trifluoride catalyst used in the isoparaffin/olefin alkylation operation can be increased by the controlled addition of water or water-forming materials to the reaction zone. The amount of introduced water either as such or in the form of an alcohol or other water-forming material is necessarily quite small, generally less than 400 ppm based on the hydrocarbon feed. Preferably, the amount of introduced water is within the range of 10 to 300 ppm and more particularly in the range of 20 to 200 ppm. Suitable water-forming materials which may be introduced into the reactor, without interfering with desired alkylation include alcohols, such as monohydric or dihydric alcohols, e.g. glycols, which upon dehydration, yield water. Of this group, particular preference is accorded the aliphatic alcohols, especially those containing 1 to 6 carbon atoms, typified by methanol, ethanol, isopropanol, t-butyl alcohol and isopentyl alcohol.

The alkylation operation may be carried out either as a batch, semi-batch, continuous or semi-continuous operation. The time of reaction will be governed by the nature of the isoparaffin and olefin reactants employed, the ratio of such reactants, the temperature and pressure conditions utilized and the particular macroreticular resin/BF_3 catalyst used.

The reactants and the catalyst may be contacted in various ways. Thus, the isoparaffin and olefin reactants may be charged to the reactor as separate streams or they may be premixed before charging to the reactor. The catalyst likewise may be first mixed with the isoparaffin or olefin before introduction into the reactor. Desirably, however, preliminary contact between the catalyst and olefin reactant should be minimized to avoid olefin polymerization. The BF_3 component of the catalyst may be premixed with the isoparaffin reactant which is then introduced into the reactor with subsequent addition of the olefin reactant. The BF_3 may further be introduced into the reaction zone separately from the introduction of the isoparaffin and olefin reactants. The catalyst may be formed in situ by prior introduction of the macroreticular resin into the reactor followed by addition of BF_3. The addition of HF, where practiced, may be effected in the same manner as the above-described addition of BF_3.

As aforenoted, the desired alkylation may be carried out as a batch or semi-batch type operation. In the case of a batch operation, the isoparaffin and olefin reactants, together with the water or water-forming material if such is being used, are charged to a closed reactor containing the catalyst, which is thereafter maintained at the desired temperature for the desired time. At the conclusion of the reaction, the hydrocarbon product mixture is withdrawn from the reactor and the alkylate product separated from unreacted materials and side products.

The alkylation process of this invention can also be carried out in continuous fashion, in which instance streams of the isoparaffin, the olefins and boron trifluoride are continuously charged to a reactor containing the macroreticular resin. In accordance with the aforementioned preferred embodiments of the invention such charge may include hydrogen fluoride and/or up to 200 ppm of water (or water equivalent of an alcohol or other water-producing material). The reactor is desirably stirred and maintained at the reaction temperature. The reaction mixture product is continuously withdrawn from the reactor, conducted to a vessel wherein BF_3 is removed as overhead and recycled to the reactor. The remaining product is conducted to a fractionator in which unreacted isoparaffin is removed as overhead and recycled to the reactor. The desired C_5+ alkylate product is withdrawn as bottoms from the fractionator. This product boils in the pentane range and below the maximum temperature usable in gasoline. Generally, the gasoline end point is about $400°F.$ The alkylate product is usually characterized by a boiling range between that of isopentane and $400°F.$ A portion of the stream coming off the vessel from which BF_3 is removed is conducted to a depropanizer, in which C_3 components are removed as overhead and heavier components, removed as bottoms, are recycled to the fractionator. Also, the isoparaffin reactant is suitably removed as a separate stream from the depropanizer and recycled to the reactor. When HF is present in the charge it is removed with the C_3 components in the depropanizer, conducted to an HF separation and recovery system, and the recovered HF is recycled for further use.

A suitable system for carrying out one embodiment of a continuous process is shown in Fig. 2. As will be realized, this described embodiment is schematic in that several items of processing

equipment have been omitted for purposes of simplification. Turning to Fig. 2, a stream containing isobutane, butenes along with some normal butane is introduced through line 10 to reactor 11 provided with a stirrer 12. The macroreticular resin has previously been introduced into the reactor. BF_3 is introduced from tank 13 through lines 14 and 15 into the reactor. The amount of BF_3 introduced is such as to exceed that necessary to saturate the resin. Catalyst slurry is removed from the reactor through outlet 16 and recycled via line 17 to the reactor. The hydrocarbon product mixture is removed from the reactor through line 18 and introduced into BF_3 stripper 19, from which BF_3 is removed as overhead through line 20 and recycled through line 21 to BF_3 tank 13. The remaining hydrocarbon product mixture is withdrawn from the BF_3 stripper through line 22. A portion of such hydrocarbon product mixture is introduced via lines 23 and 24 to fractionator 25. Unreacted isobutane is removed as overhead through line 26 and recycled through line 27 to the reactant feed stream line 10. Desired C_5+ alkylate product is withdrawn from the bottom of fractionator 25 through line 28. Any normal butane may be withdrawn from the fractionator through line 29. The remaining portion of the hydrocarbon product mixture passing through line 22 from BF_3 stripper 19 is conducted through line 30 to depropanizer 31, from which propane is removed as overhead through line 32. Heavier components are removed as bottoms through line 33 and recycled via lines 34 and 24 to fractionator 25. Isobutane is removed from depropanizer 31 through line 35 and recycled through lines 36 and 27 to the initial reactant feed line 10.

When the reaction is carried out in the presence of a small amount (less than 400 ppm) of water and alcohol, or alcohol-isobutane solution, is introduced into the system through line 9.

A suitable system for carrying out the continuous process is shown in Fig. 3. As will be realized, this described embodiment is schematic in that several items of processing equipment have been omitted for purposes of simplification.

Turning to Fig. 3, a stream containing isobutane and butenes along with some normal butane is introduced through line 10 to reactor 11 provided with a stirrer 12. The macroreticular resin has previously been introduced into the reactor. BF_3 is introduced from tank 13 through 14 and 15 into the reactor. Likewise, HF is introduced from tank 16 through lines 17 and 18 into the reactor. Catalyst slurry is removed from the reactor through outlet 19 and recycled via line 20 to the reactor. The hydrocarbon product mixture is removed from the reactor through line 21 and introduced into BF_3 stripper 22, from which BF_3 is removed as overhead through line 23 and recycled through line 24 to BF_3 tank 13. The remaining product mixture is withdrawn from the BF_3 stripper through line 25 and a portion introduced via lines 26, 27 and 28 to fractionator 29. Unreacted isobutane is removed as overhead through line 30 and recycled through line 31 to the reactant feed stream 10. Desired C_5+ alkylate product is withdrawn from the bottom of fractionator 29 through line 32. Any normal butane may be withdrawn from the fractionator through line 33. The remaining portion fo the hydrocarbon product mixture passing through line 26 from BF_3 stripper 22 is conducted through line 34 to depropanizer 35, from which propane and HF are removed as overhead through line 36. Heavier components are removed as bottoms through line 37 and recycled via lines 38 and 28 to fractionator 29. Isobutane is removed from depropanizer 35 through line 39 and recycled through lines 40 and 31 to the initial reactant feed line 10. The propane and HF mixture removed from depropanizer 35 via line 36 is conducted by line 41 to separator 42. The separated HF is removed from separator 42 by line 43 and recycled via lines 44 and 45 to the HF tank 16. The remaining propane from separator 42 is conducted through line 46 to the HF stripper 47 to remove additional HF. The HF is removed from HF stripper 47 via line 48 from which it passes in to separator 49. The separated HF is conducted through lines 50, 51 and 45 to the HF tank 16 from which it is recycled via lines 17 and 18 to feed line 10. The hydrocarbon rich phase is removed from separator 49 via line 52 and passed into HF stripper 47. Propane product is removed from HF stripper 47 via line 53.

Upon carrying out isoparaffin/olefin alkylation with the above-described catalyst, it has been observed that both the yield and quality of desired alkylate product declines with time on stream. Thus, the C_5-C_{12} yield for isobutane/butene-2 alkylation diminished with duration of the operation. Also, the trimethylpentane content of the C_5-C_{12} alkylate decreased with time on stream. Such reduction in yield and quality of the desired alkylate has been established as being attributable to aging of the macroreticular acid cation exchange resin of the catalyst employed.

It has been found that regeneration of the spent macroreticular acid cation exchange resin can be effected by extraction thereof with a polar solvent under suitable conditions of time and temperature. Such treatment has been discovered to restore very substantially or completely the activity of the resin, in conjunction with boron trifluoride, for further isoparaffin/olefin alkylation operation.

The polar solvents suitable for use in effecting the desired regeneration include water, ethers, alcohols, including glycols, and ketones, such as acetone.

Particular preference is accorded low molecular weight C_1 to C_5 alcohols such as methanol, ethanol, butanol, propanol, isopropanol, isobutanol, pentanol and isopentanol. It has been established that the solvent employed is necessarily polar. Non-polar solvents such as aromatic

hydrocarbons, e.g. benzene, and paraffinic hydrocarbons, e.g. n-hexane, were, as hereinafter demonstrated, not effective in achieving the desired regeneration. In operation, the spent resin is contacted by slurrying or continuous extraction with the selected polar solvent. The duration of such contact will depend on the particular macroreticular resin undergoing treatment, the extent of its deactivation and the nature of the solvent employed. Generally, contact between the spent resin and polar solvent will be maintained for 1/4 to 10 hours at a temperature below the boiling point of the solvent and usually within the approximate range of 15°C. to 130°C. The resin so treated is separated from the polar solvent, thereafter dried and is then ready for re-use. It is contemplated that regeneration of the spent resin may take place outside the reaction zone or may be accomplished utilizing in situ techniques. Also, regeneration may be effected as a batch type operation or in a continuous manner as part of an overall continuous alkylation operation.

A suitable system for carrying out such operation is shown in Fig. 4. As will be realised, this described embodiment is schematic in that several items of processing equipment have been omitted for purposes of simplification. Turning to Fig. 4, a stream containing isobutane, butenes along with some normal butane is introduced through line 10 to reactor 11 provided with a stirrer 12. The macroreticular resin has previously been introduced into the reactor. BF_3 is introduced from tank 33 through lines 14 and 15 into the reactor. The amount of BF_3 introduced is such as to exceed that necessary to saturate the resin. Catalyst slurry is removed from the reactor through outlet 16 and recycled via line 17 to the reactor. A slip stream of catalyst and alkylate is removed via line 18 and conducted to a regenerator 19. Polar solvent is introduced into regenerator 19 through line 20. Contact of the catalyst-alkylate slurry and polar solvent takes place in regenerator 19. A combined stream of solvent and alkylate-catalyst slurry is removed from regenerator 19 through line 21 and conducted into distiller 22 from which the polar solvent is removed as overhead vapour through line 23 and conducted to condenser 24 wherein the solvent vapour is condensed to liquid. Condensed liquid passes from condenser 24 through line 25 and is recycled to solvent inlet line 20. A stream of regenerated catalyst and alkylate is removed from distiller 22 through line 26 and recycled to reactor 11. Light boiling material is removed as overhead through conduit 27 and conducted to line 26. Residue material is removed from distiller 22 through line 28. The hydrocarbon product mixture is removed from a reactor through line 29 and introduced into BF_3 stripper 30 from which BF_3 is removed as overhead through line 31 and recycled through line 32 to BF_3 tank 33. The remaining hydrocarbon mixture is withdrawn from the BF_3 stripper through line 34. A portion of such hydrocarbon product is introduced via lines 35 and 36 to fractionator 37. Unreacted isobutane is removed as overhead through line 38 and recycled through line 39 to the reactant feed stream line 10. Desired C_5+ alkylate product is withdrawn from the bottom of fractionator 37 through line 40. Any normal butane may be withdrawn from the fractionator through line 41. The remaining portion of the hydrocarbon product mixture passing through line 34 from BF_3 stripper 30 is conducted through line 42 to depropanizer 43, from which propane is removed as overhead through line 44. Heavier components are removed as bottoms through line 45 and recycled via lines 46 and 36 to fractionator 37. Isobutane is removed from depropanizer 43 through line 47 and recycled through lines 48 and 39 to the initial reactant feed line 10.

A particularly effective system for carrying out the desired alkylation is a semi-continuous operation. It has, in accordance with this invention, been unexpectedly found that the aging rate of the macroreticular acid cation exchange resin/boron trifluoride used for the isoparaffin/olefin alkylation can be considerably reduced by means of a semicontinuous, rather than a continuous operation. Thus, by way of comparison, semi-continuous isobutane/butene-2 alkylation utilizing the described catalyst produced an alkylate containing 47 percent trimethylpentanes (bromine number = 0.7) with a yield of 1.95 grams C_5-C_{12}/gram olefin converted after the catalyst had processed 109 grams hydrocarbon/gram resin (18.2 grams olefin converted/gram resin). In contrast, continuous isobutane/butene-2 alkylation with the identical resin/BF_3 catalyst under like conditions produced an alkylate which contained only 29 percent trimethylpentanes (bromine number was 5.9) with a yield of 1.3 gram C_5-C_{12}/gram olefin converted after the catalyst had processed 68.4 grams of hydrocarbon/gram resin (11.4 grams olefin converted/gram resin). Most noteworthy was the fact that the semi-continuous operation significantly reduced the aging rate of the catalyst. In carrying out the semi-continuous operation, the isoparaffin reactant is charged to the reactor, which contains the macroreticular resin. The required amount of BF_3, i.e. an amount in excess of that needed to saturate the resin, is then charged to the reactor. The resulting mixture is stirred for a suitable period of time, e.g. about 30 minutes, to insure good contact between the macroreticular acid cation exchange resin, isoparaffin and boron trifluoride. After such mixing period, the olefin reactant is charged continuously at a desired rate, e.g. 2.6 grams olefin/gram resin/hour. The alkylation reaction is then continued for a suitable period of time, e.g. about 1 hour, after which the reactor contents, excluding the macroreticular resin, are removed and the desired alkylate product separated therefrom. Then, the whole cycle is repeated.

A suitable system for carrying out the described semi-continuous method of operation is shown in Fig. 5. As in the case of Fig. 2, it will be realised that the semi-continuous method of operation

shown could be considered to be schematic in nature since several items of processing equipment have been omitted to simplify the illustrated operation. Turning now to Fig. 5, isobutane is introduced via line 40 to reactor 41 equipped with a stirrer 42. The macroreticular resin had previously been introduced into reactor 41. BF_3 is introduced into reactor 41 from tank 43 via lines 44 and 45. The resulting mixture is stirred to insure thorough mixing of the isobutane reactant, the macroreticular resin and BF_3. Thereafter, butenes are introduced through inlet line 40 to the reactor. After a suitable catalyst settling time, the hydrocarbon product mixture is withdrawn from the reactor through line 46 and introduced via line 47 to product tank 48. The mixture is then conducted via line 49 to BF_3 stripper 50 wherein BF_3 is removed as overhead through line 51 and recycled through line 52 to BF_3 tank 43. The bottoms product from BF_3 stripper 50 is removed via line 53. A portion of such mixture is conducted via lines 54 and 55 to fractionator 56. Isobutane is removed as overhead via line 57 and recycled through line 58 to inlet feed line 40. The C_5+ alkylate product is withdrawn from bottoms fractionator 56 through line 59. Any normal butane is removed via line 60. Another portion of the hydrocarbon product mixture passing through line 53 from BF_3 stripper 50 is conducted via line 61 to depropanizer 62, from which propane is removed as overhead via line 63. Isobutane is removed from depropanizer 62 through line 64 and recycled via lines 65 and 58 to feed line 40. Higher boiling materials are removed from bottoms depropanizer 62 through line 66 and recycled via lines 67 and 55 to fractionator 56. A second reactor 68 also equipped with a stirrer 69 is operated in tandem with reactor 41 with the reactants being introduced via lines 70 and 71 and BF_3 being introduced via line 72 and isobutane recycle being introduced via line 73. The product from reactor 68 is removed via line 74 and conducted via line 47 to product tank 48, from which the operation is as described above. As noted, the dual reactor system in the described semi-continuous operation is operated in tandem utilizing suitable reactor cycles in each vessel. A suitable schedule for semi-continuous operation is shown below:

Step		Time, min.	Step R-1	Step R-2
1.	Charge with isobutane	10	1	4
2.	Charge with BF_3	5	2	4
3.	Stir with resin	30	3	4
4.	Charge olefin	60	4	5,6,1,2,3
5.	Catalyst settling time	8	5	4
6.	Drain hydrocarbon	7	6	4

Operation in a semi-continuous fashion has been found to result in an improvement in product quality and to reduce the aging rate of the catalyst as contrasted with a continuous manner of operation. The beneficial effect of semi-continuous operation on alkylate yield, compared with a continuous method of operation, is shown in Fig. 6. Referring to this figure, data are presented depicting the yield of C_5-C_{12} alkylate/gram olefin as a function of catalyst age, gram olefin charge/gram resin. The data shown result from isobutane-butene-2 alkylation using Amberlyst XN-1010/boron trifluoride catalyst at a temperature of 40°C. and utilizing an isobutane to butene-2 molar ratio of 5 to 1. It will be seen from Fig. 6 that semi-continuous operation produced an alkylate with a constant yield of 1.95 grams C_5-C_{12}/gram olefin (theoretically maximum yield is 2.03 gram C_5+/gram olefin for isobutane/butene alkylation) for a catalyst age of 26 grams olefin charge/gram resin. This is to be contrasted with a continuous operation carried out under like conditions with like reactants and catalyst in which the C_5-C_{12} yield dropped to 1.3 gram C_5-C_{12}/gram olefin as the catalyst aged to 11.4 grams olefin charge/gram resin.

The benefits of semi-continuous operation in terms of product quality utilizing the above reactants and the same process conditions are shown in Fig. 7. Semi-continuous operation affords production of higher quality alkylate (as determined by trimethylpentane content of alkylate) at all catalyst ages when compared with a continuous operation. Such is further substantiated by a comparison of bromine numbers. A low bromine number indicates alkylation while a high bromine number denotes polymerisation. For semi-continuous operation, the product produced at a catalyst age of approximately 26 grams olefin/gram resin had a bromine number less than 0.7; whereas for continuous operation at a catalyst age of approximately 11 grams olefin/gram resin, the product produced during the entire course of operation had a bromine number of 5.9.

Description of Specific Embodiments

The following examples will serve to illustrate the invention without limiting the same.

Examples 1 to 20 were carried out in a 300 ml. stainless steel stirred autoclave under pressure using a semi-batch type operation. In accordance with a standard procedure, 7 grams of macroreticular sulfonic acid ion exchange resin were placed in the reactor and 93 grams of isoparaffin, i.e. isobutane, were charged into the reactor under N_2 pressure. Then, about 6–7 grams of BF_3 were charged and the system was stirred at 1800 R.P.M. After the desired

temperature was reached, the olefin, i.e. butene, was fed in slowly during the duration of the run. An on-line chromatograph which was equipped with a flame-ionization detector and a digital integrator, was employed to monitor the course of alkylation.

At the end of the run, the product was discharged under a N_2 flow into a metal bomb which
5 was kept at −73°C. The product was warmed to room temperature and transferred to the   5
atmospheric pressure weathering system which consisted of two BF_3-scrubbers, a solenoid valve and a ten-liter gas collector which was equipped with an automatic pressure controller. Both the weathered liquid and the weathered gas were analysed on a SCOT PAK column (100' x 0.02") coated with squalane. The program used for the analysis was to hold the column at 45°C. for six
10 minutes, then program to 120°C. at 2°C./min. and held at 120°C. until the analysis was 10
completed. The weathered gas contained less than 2 percent and generally less than 1 percent of the total C_2 produced, depending on conditions and the particular resin used.

All octane ratings were determined using the minimicro octane test unless otherwise specified. All octane numbers were determined clear. The RON of the weathered liquid was converted for
15 the C_4^- content to obtain the RON of C_5+ in the weathered liquid. The C_5+ yield is defined as 15
weight of C_5+ produced per unit weight of butene converted. The C_5+ yield was calculated on the basis of the total weight of liquid collected at the end of each run.

Three different methods of pretreating the resins were used:

(1) Method A: 220 grams of the dry resin were refluxed for four hours with 5 percent NaOH
20 solution (1 liter), washed several times with water, soaked in 20 percent H_2SO_4 solution (1 liter) 20
overnight with stirring, filtered, soaked for 15 minutes four times in 20 percent H_2SO_4 solution (500 ml. each time), filtered, washed with distilled water until pH matched that of distilled water, and finally rinsed with 500 ml. of acetone and 1 liter of water. The resulting resin was stored in water.

25 (2) Method B: 50 grams of resin were washed chromatographically with methanol until the 25
eluent was clear. The resin was further eluted with 3 liters of methanol at a flow rate of 12 cc/min., rinsed with 3 liters of water, then washed with 1.5 liters of 4 percent NaOH solution, rinsed with at least 5 liters of water at 30 cc/min., exchanged with 2 liters of 15 percent H_2SO_4 solution at a flow rate of 12 cc/min. and finally rinsed with a large amount of distilled water until
30 free of acid. The resin was stored in water.   30

(3) Method C: 50 grams of resin were washed chromatographically with methanol and toluene (separately in a number of repeated cycles) until the eluent was clear. The resin was then washed with water, rinsed with about 400 cc of 4 percent NaOH solution, washed with water and then exchanged with about 400 cc of 15 percent H_2SO_4 solution and finally rinsed with a large amount
35 of distilled water until free of acid. The resin was stored in water.   35

While pretreatment of the resin was, in most cases, desirable and particularly the pretreatment of Method B, it is not considered essential, in every instance, to the success of the described alkylation process.

40 The pretreated resin was dried in vacuum for 3 hours at 120°C. prior to use. All resins were
                                                                                         40
ground to pass through 100 mesh unless otherwise specified.

Detailed results are set forth in Table I below of a series of isobutane/trans-2-butene alkylation experiments using Amberlyst-15 alone, BF_3 alone, Amberlyst-15 with a trace of BF_3, Amberlyst-15/BF_3 in 1:1 complex form and Amberlyst-15/BF_3 with an excess of BF_3.

Table I

	1	2	3	4	5
Example No.	1	2	3	4	5
Catalyst	Amberlyst-15/BF_3	Reused Catalyst from Ex. 1	Reused Catalyst from Ex. 2 plus 6.8 g. BF_3	BF_3 only	Amberlyst-15 only
Temperature, °C.	40	40	40	40	40
Pressure, psig	161	160	255	230	160
Reactor Mode	Semi-Batch	Semi-Batch	Semi-Batch	Semi-Batch	Semi-Batch
Run Duration, Hr.	5	5	5	5	5
Resin Pretreatment Method	C	C	C	C	C
Catalyst Loading:					
Resin, gm	13.9	13.9	13.9	0.0	13.0
BF_3, gm	4.7	<4.7(1)	(<4.7)(1)+6.8	4.0	0.0
C_4=Space Velocity:					
gC_4=/g Resin/hr.	0.18	0.18	0.18	—	0.19
Wt. of H.C. Feed					
i-C_4, gm	93.0	93.0	93.0	93.0	93.0
2-C_4=, gm	12.36	12.36	12.36	12.36	12.36
External i-C_4/C_4= Ratio (2)	7.5	7.5	7.5	7.5	7.5
gm Resin/gm-i-C_4	0.15	0.15	0.15	—	0.14
Olefin Conversion, %	100.0	99.95	100.0	96.92	
C_5+ Yield, gC_5+/gC_4=Conv.	1.21	0.94	1.92	1.16	
Wt. % of C_8 in C_5	56.55	42.30	79.15	47.87	
Bromine No. of Weathered Liq.	—	—	<0.1	25.53	
RON of C_5+	—	—	95.5	—	
C_5+ Paraffin Dist., mol %					
C_9+	19.53	37.02	6.35	18.35	
C_8	54.75	43.47	76.29	44.61	
C_7	5.94	4.22	4.48	8.60	
C_6	7.20	6.02	4.41	11.13	
C_5	12.58	9.14	8.47	17.31	
C_8 Paraffin Dist., mol %					
Trimethylpentanes	84.12	81.39	74.51	73.07	
Dimethylhexanes	15.85	18.02	24.61	26.40	
Methylheptanes	0.03	0.32	0.88	0.51	
n-Octane	0.0	0.27	0.0	0.02	

(1) Residual BF_3 in the used resin.
(2) The external i-C_4/C_4= ratio is defined as the ratio of isobutane to the total butene pumped during the course of the run.

1,432,720

The above results demonstrate that the macroreticular resin or BF_3 alone gave primarily undesired polymerization while a combination with excess BF_3 was an effective catalyst. The results of Example 3 further showed that the resin/BF_3 complex could be prepared in situ by mixing BF_3 and the resin in isobutane liquid for about an hour prior to feeding olefin into the reactor.

The effects of the amount of BF_3 and Na^+ on isobutane/trans-2-butene alkylation is shown by the results set forth in Table II below:

Table II

Example No.	6	7	8	9
Catalyst	Amberlyst 15/BF₃	Reused Catalyst from Ex. 6 plus 3.3 g. BF₃	Amberlyst-15 (Na+ form)/BF₃	Amberlyst-15/BF₃ (ultra dry)
Temperature, °C.	40	40	40	40
Pressure, psig	175	210	190	240
Reactor Mode	Semi-Batch	"	"	"
Run Duration, Hr.	1	"	"	"
Resin Pretreatment Method	C	"	"	"
Catalyst Loading:				
Resin, gm	7.0	7.0	7.0	7.0
BF₃, gm	3.9	(<3.9)(1) + 3.3	6.3	6.9
C₄= Space Velocity: gC₄=/g Resin/Hr.	2.6	2.6	2.6	2.6
Wt. of H.C. Feed				
i-C₄, gm	93.0	93.0	93.0	93.0
2-C₄=, gm	18.13	18.13	18.13	18.13
External i-C₄/C₄= Ratio	5.1	5.1	5.1	5.1
gm Resin/gm-i-C₄	0.075	0.075	0.075	0.075
Olefin Conversion, %.	99.2	100.0	100.0	100.0
C₅+ Yield, gC₅+/gC₄= Conv.	1.02	1.95	0.93	1.99
Wt. % of C₈ in C₅	49.98	54.75	36.03	56.16
RON of C₅+	—	90.0	41.1	92.3
Bromine No. of Weathered Liq.	<0.1	<0.1	<0.1	<0.1
C₅+ Paraffin Dist., mol %				
C₉+	29.06	18.34	50.55	20.08
C₈	50.25	50.38	39.25	54.55
C₇	4.92	7.52	3.00	6.44
C₆	6.58	8.20	3.30	7.37
C₅	9.19	13.56	3.84	11.57
C₈ Paraffin Dist., mol %				
Trimethylpentanes	81.27	74.19	80.96	75.72
Dimethylhexanes	18.73	25.17	19.04	23.63
Methylheptanes	0.0	0.64	0.0	0.65
n-Octane	0.0	0.0	0.0	0.0

(1)   Residual BF₃ in the used resin.

From the above it is seen that it is desirable to employ BF_3 in an amount in excess of that needed to saturate the resin. Particularly, this is evident from a comparison of the results of Examples 1, 3, 6 and 7 below:

Example No.	1	3	6	7
Olefin Space Velocity	0.18	0.18	2.6	2.6
Equivalent Ratio of (total)* BF_3 to $-SO_3H$	1.0	2.1	1.7	2.4
Olefin Conversion, %	100	100	99.2	100
C_5+ Yield	1.21	1.92	1.02	1.95

* Including BF_3 in the vapour phase, the liquid hydrocarbon phase and the resin.

The C_5+ yields shown above indicate that alkylation activity dominates when the equivalent ratio of total BF_3 to $-SO_3H$ exceeds 2 but that polymerisation predominates at equivalent ratios less than 2. Thus, an equivalent ratio of total BF_3 to $-SO_3H$, i.e. the acid group, of between 2 and 3 is desirably employed.

The necessary participation of H^+ in the desired alkylation is shown from the results of Examples 7 and 8. In the latter example, the sodium form of the macroreticular resin was used to determine if the H^+ on the $-SO_3H$ group was a necessary factor. The results of Examples 7 and 8 are condensed below:

Example No.	7	8
Cation in Resin	H^+	Na^+
Olefin Conversion, %	100	91
C_5^+ Yield	1.95	0.93

These comparative data establish that the acid group is essential for effecting the desired alkylation.

The results of using various macroreticular acid cation exchange resins, together with a microreticular resin, are summarised in Table III below:

Table III

	10	11	12	13	14	15	16
Example No.	10	11	12	13	14	15	16
Catalyst	Amberlyst-15/BF₃	Amberlyst-XN-1010/BF₃	Amberlyst-XN-1008/BF₃	Amberlyst-XN-1011/BF₃	Amberlite-200/BF₃	Amberlyst-XN-1005/BF₃	Amberlite-IR-120H/BF₃
Type	Macroreticular	Macroreticular	Macroreticular	Macroreticular	Macroreticular	Macroreticular	Microreticular
Temperature, °C.	40	40	40	40	40	40	40
Pressure, psig	225	230	230	230	225	240	245
Reactor Mode	Semi-Batch	"	"	"	"	"	"
Run Duration, Hr.	1	"	"	"	"	"	"
Resin Pretreatment Method	"B"	"	"	"	"	"	"
Catalyst Loading:							
Resin, gm	7.0	7.0	7.0	7.0	7.0	7.0	7.0
BF₃, gm	6.7	6.9	6.2	6.2	6.9	6.3	6.8
$C_4^=$=Space Velocity: gm $C_4^=$/g Resin/Hr.	2.6	2.6	2.6	2.6	2.6	2.6	2.6
Wt. of H.C. Feed							
i-C_4, gm	93.0	93.0	93.0	93.0	93.0	93.0	93.0
2-$C_4^=$, gm	19.34	18.13	18.13	18.13	18.13	18.13	18.13
External i-C_4/$C_4^=$=Ratio	4.8	5.1	5.1	5.1	5.1	5.1	5.1
gm Resin/gm-i-C_4	0.075	0.075	0.075	0.075	0.075	0.075	0.075
Olefin Conversion, %	100.0	100.0	100.0	100.0	100.0	100.0	100.0
C_5^+ Yield, gC_5^+/g$C_4^=$=Conv.	1.89	1.88	1.86	1.88	1.91	1.76	1.52
Wt. % of C_8 in C_5^+	66.08	78.93	53.83	60.73	64.30	65.45	41.48
Bromine No. of Weathered Liq.	<0.1	<0.1	1.0	0.1	0.1	0.1	7.4
RON of C_5^+	94.5	96.5	92.4	92.3	93.7	95.6	93.2
C_5^+ Paraffin Dist, mol %							
C_9	15.55	9.49	17.53	15.49	17.96	16.811	33.07
C_8	64.81	77.91	50.95	58.28	63.79	64.57	41.39
C_7	5.36	3.85	8.00	6.97	5.66	4.95	6.29
C_6	5.79	3.24	8.85	7.37	5.83	5.31	7.49
C_5	8.49	5.51	14.66	11.89	6.76	8.36	11.77
C_8 Paraffin Dist, mol%							
Trimethylpentanes	79.06	88.33	73.12	75.52	80.87	86.39	77.00
Dimethylhexanes	20.46	11.67	26.11	23.78	18.74	13.61	22.36
Methylheptanes	0.48	0.0	0.78	0.70	0.39	0.0	0.60
n-Octane	0.0	0.0	0.0	0.0	0.0	0.0	0.03

It will be seen from the above data that the alkylate and octane number selectivities for trimethylpentane increase with increasing surface area of the resin employed. Amberlyst XN-1010 with the highest surface area and porosity, the smallest pore diameter and the lowest surface acid concentration was the most selective resin observed and produced the highest quality alkylate with a RON clear of 96.5. In marked contrast to the results obtained utilising the macroreticular resin, the microreticular resin of extremely low surface area and porosity and possessing a very much larger surface acid concentration gave a lower C_5^+ yield, lower selectivity for trimethylpentane and a higher bromine number for the product denoting formation of unwanted olefinic products rather than desired alkylation.

The effect of surface area of resin on the selectivity of trimethylpentane in C_5+ and C_8 and the octane number of C_5+ alkylate are depicted in Fig. 8 and Fig. 9. From these data, it will be seen that the surface area of the resin employed should desirably be above 20 square meters per gram and generally between 30 and 800 square meters per gram.

A series of experiments showing the effect of temperature was carried out. In these examples, isobutane/trans-2-butene alkylation over Amberlyst XN-1010/BF_3 catalyst was studied at $0°$, $20°$, $40°$ and $60°C$. The results are summarised below:

Example No.	17	18	19	20
Temperature, °C	$0°$	$20°$	$40°$	$60°$
Wt. % of TMP in C_5+	90.3	80.6	69.7	50.6
Wt. % of TMP in C_8	97.1	93.5	88.3	77.5
Wt. of C_9+ in C_5+	4.2	9.2	11.6	20.7
RON clear of C_5+ alkylate	101.9	99.1	96.5	96.0

As will be seen from the above, the selectivity for trimethylpentane and the RON of C_5+ alkylate increase sharply with decreasing temperature. An alkylate with a RON clear of 101.9 was produced at $0°C$. and an olefin space velocity of 2.6.

The effect of temperature on weight percent of C_8 in C_5+ and mole percent of trimethylpentane in C_8 are depicted in Fig. 10, while the effect of temperature on octane number of the C_5+ alkylate is shown in Fig. 11. It is evident that temperatures in the lower range, between $-20°C$. and $+20°C$., overall are particularly preferred.

Results showing the importance of the resin water content to the ability of a macroreticular acid cation exchange resin/boron trifluoride catalyst to effect an isobutane/butene-2 alkylation are set forth in Table IV below:

Table IV

Example	21	22	23
Water Content of Resin, wt. %	Anhydrous (0%)	6.7	25
Olefin Space Velocity, $gC_4=$/g resin-hour	2.4	2.6	2.1
Olefin Conversion, %	99	100	2
C_5+ Yield, g C_5+/g $C_4=$	0.5	1.96	<0.1
Trimethylpentanes in C_5+, wt. %	42	91.4	—
C_9+ in Alkylate, mole %	60	7.6	—

The above-tabulated experiments were carried out at a temperature of $0°C$. in a semi-batch reactor in which Amberlyst XN-1010, isobutane and boron trifluoride were initially placed and to which butene-2 was subsequently added continuously for one hour. The results of Example 21 show that anhydrous (azeotropically dried with normal heptane) Amberlyst XN-1010/BF_3 does not effectively catalyze the desired alkylation, as evidenced by the low yield of 0.5 gram C_5+/gram of C_4 olefin converted (theoretical yield = 2.03 gram C_5+/gram of C_4 olefin converted) and the large quantity of C_9+ material in the alkylate. The results of Example 22 show that if the resin contains about 7 weight percent water, Amberlyst XN-1010/BF_3 is an effective alkylation catalyst producing an alkylate which contains 91.4 weight percent trimethylpentanes with an alkylate yield of 1.96 grams C_5+/gram C_4 olefin. The results of Example 23 show that too much water in the resin can detrimentally affect the performance of an Amberlyst XN-1010/BF_3 catalyst, the resin component of which contained 25 weight percent water. Only 2 percent conversion of the olefin was achieved under essentially identical conditions. These data show that there is an optimum

water content of the resin in the approximate range of 0.5 to 20 weight percent, which must be maintained in order that the acidic cation exchange resin/boron trifluoride catalyst is capable of performing with peak activity and selectivity.

During continuous alkylation of the isoparaffin/olefin feed with a macroreticular acid cation exchange resin/boron trifluoride catalyst, the product yield and selectivity declined with use. This decline is considered to be associated, in part, with removal of water from the resin. A method of counteracting this activity decline by maintaining a small controlled amount of water, less than 400 ppm, as a result of introduction of water on a water-forming material into the reaction zone has, in accordance with the present invention, been found, as will be evident from the experimental data hereinafter set forth.

All experiments were performed in a continuous stirred tank reactor. For runs without the addition of water or a water-forming material, isobutane, olefin and boron trifluoride were charged continuously to the stirred reactor, to which the macroreticular acid cation exchange resin had been added. Alkylate, unreacted isobutane, olefin and boron trifluoride were continuously withdrawn from the reactor. For runs with addition of a controlled quantity of water as a result of dehydration of an alcohol, an isobutane/alcohol solution of desired concentration was fed at the desired rate into the isobutane/olefin feed line for the duration of the run. Other input/output streams to and from the reactor were conducted as described above. All runs were made at $0°C.$, olefin WHSV of 2.5 grams olefin/gram resin/hour with a 5/1 isobutane/butene-2 feed. The macroreticular cation exchange resin Amberlyst XN-1010 was used in the acid form and contained about 6 weight percent water.

The effect of the addition of a small amount of alcohol, e.g. methanol, to the above reaction mixture of isobutane and butene-2 in the presence of Amberlyst XN-1010/BF_3 catalyst at $0°C.$ is shown in Fig. 12 wherein alkylate yield is plotted against time on stream. Curve A shows the performance of the catalyst when the feed contains no added water. With the addition of 18 ppm of water equivalent in the feed, the performance of the catalyst, as shown by Curve B, evidences substantial improvement. Upon increase in the water equivalent in the feed to 72 ppm, as illustrated by Curve C, still further improvement in catalyst stability was observed. The fact that large quantities of water equivalent in the feed can have a detrimental effect on catalyst performance is evidenced by Curve D wherein the feed contained 500 ppm of water equivalent.

The benefits of adding water (via methanol) to the feed in terms of product quality is shown by Fig. 13. Product quality is determined by the trimethylpentane content of the C_5-C_{12} alkylate. The addition of small quantities, i.e. less than 72 ppm, of water equivalent to the feed resulted in improved product quality, particularly at long times on stream. The detrimental effect on product quality of large quantities of water equivalent is clearly shown by Curve D.

The results shown graphically in Figs. 14 and 15 compare the effectiveness of water derived from methanol with that from t-butyl alcohol in terms of C_5-C_{12} yield and product quality respectively. At a water equivalent level of 72 ppm, Curve A shows that the source alcohol has no significant effect on catalyst performance. At a water equivalent level of 500 ppm, water derived from t-butyl alcohol shown by the results of Curve C appears to be slightly more effective than the corresponding results achieved with methanol as shown by Curve B in terms of both product yield (Fig. 14) and product quality (Fig. 15).

From the above results, it will be seen that the addition of methanol or t-butyl alcohol to give a water equivalent of 72 ppm water, based on hydrocarbon feed, to the reaction zone during continuous alkylation of isobutane/butene-2 feed using Amberlyst XN-1010/BF_3 catalyst increased the catalyst's cycle life from 63 hours to 90 hours, at which point the C_5-C_{12} yield in both cases was 1.5 grams C_5-C_{12} alkylate/gram butene-2 converted. At equal times on stream of 70 hours, alkylation with 72 ppm water equivalent of methanol fed continuously to the reaction zone, proceeded to give a C_5-C_{12} alkylate which contained 67 weight percent trimethylpentanes with a C_5-C_{12} yield of 1.82 grams C_5-C_{12}/gram butene-2 converted, whereas without addition of water or its precursor, the corresponding quantities were 60 weight percent and 1.1 gram C_5-C_{12}/gram butene-2 converted.

The following example serves to show the beneficial effect achieved by water injection:

Example 24

Amberlyst XN-1010 ion exchange resin/boron trifluoride catalyst was aged by continuously alkylating a 2/1 isobutane/butene-2 feed at $0°C.$ and butene-2 WHSV of 2.5 gram olefin/ gram resin/hour for 30 hours at which point the C_5-C_{12} yield declined from 1.85 to 1.35 gram C_5-C_{12}/gram butene-2 converted and the trimethylpentane content of the C_5-C_{12} alkylate declined from 81 to 51 weight percent.

The liquid and gaseous contents of the reactor were drained and isobutane and boron trifluoride were then charged to the reactor. As soon as the reactor attained a temperature of $0°C.$, 0.06 of g water/g resin was injected directly into the reactor all at once and 2/1 isobutane/ butene-2 feed and boron trifluoride were fed continuously to the reactor as above. After 17 hours on stream, the C_5-C_{12} yield declined from 1.71 to 1.66 gram C_5-C_{12}/gram butene-2 converted and the trimethylpentane content of the C_5-C_{12} alkylate decreased from 67 to 53 weight percent.

Example 25

Amberlyst-15 ion exchange resin/boron trifluoride catalyst was aged by continuously alkylating a 10/1 isobutane/butene-2 feed at $0°C$. and butene 2 WHSV of 2.5 grams olefin/gram resin/hour for 49 hours on stream at which point the C_5-C_{12} yield declined from 1.85 to 1.35 grams C_5-C_{12}/gram of butene-2 converted and the trimethylpentane content of the C_5-C_{12} alkylate declined from 71 weight percent to 51 weight percent.

Regeneration of this spent resin catalyst was effected by slurrying with methanol (methanol/ resin = 25 grams/gram) for 4 hours at $40°C$., removing the bulk of the methanol from the resin by vacuum filtration, drying the resin at $40°C$. under 25 in. mercury vacuum for 5 hours followed by room temperature drying under 25 in. mercury vacuum for 16 hours. The regenerated resin produced an alkylate with a C_5-C_{12} yield of 1.75 grams C_5-C_{12}/gram of butene-2 and a trimethylpentane content of 69 weight percent at 20 hours on stream under the above alkylation conditions.

Example 26

Amberlyst XN-1010 cation exchange resin/boron trifluoride catalyst was aged by continuously alkylating a 10/1 isobutane/butene-2 feed at $0°C$. and butene-2 WHSV of 2.5 grams olefin/gram resin/hour.

During alkylation, the C_5-C_{12} yield declined from 2.00 to 0.22 grams C_5-C_{12}/gram of butene-2 and the trimethylpentane content of the C_5-C_{12} alkylate declined from 86 weight percent to 73 weight percent.

Regeneration of this aged resin catalyst was accomplished by extraction in a Soxhlet apparatus. Nine grams of the aged resin were extracted in such apparatus for 3 hours with methanol (400 ml.), then 2 hours with hexane (400 ml.), followed by 1 hour with methanol (400 ml.) and finally with water for 1 hour. All extractions were performed at reflux temperature. The resulting resin was filtered and dried under vacuum at $120°C$. for 3 hours prior to use.

The regenerated resin produced an alkylate after 3 hours on stream under the above alkylation conditions with a C_5-C_{12} yield of 1.93 grams C_5-C_{12} gram of butene-2 and a trimethylpenane yield of 76.5 weight percent.

Example 27

Amberlyst XN-1010 cation exchange resin/boron trifluoride catalyst was aged by continuously alkylating a 10/1 isobutane/butene-2 feed at $0°C$. and butene-2 WHSV of 2.5 grams olefin/gram resin/hour.

During alkylation, C_5-C_{12} yield declined from 1.88 to 0.7 grams C_5-C_{12}/gram of butene-2 and the trimethylpentane content of the C_5-C_{12} alkylate declined from 85 weight percent to 56 weight percent.

The aged resin catalyst (5 grams) was contacted with hexane (250 ml.) in a Soxhlet apparatus for 4 hours. Excess hexane was removed from the extracted resin by drying at $100°C$. Water was restored to the resin by equilibrating it with air at 100 percent relative humidity for 2 days. The water content of the resin was reduced to the desired level by drying the resin for 3 hours at $120°C$. under 25 in. mercury vacuum.

The resin so treated was tested for rejuvenation by carrying out a semi-batch reactor isobutane/butene-2 alkylation test at $0°C$. with a butene-2 WHSV of 2.4 grams butene-2/gram resin/hour and a cumulative isobutane/butene-2 ratio of 5.36 mole/mole. After 1 hour of reaction time under the above conditions, the treated resin produced a C_5-C_{12} alkylate with a yield of 0.5 gram C_5-C_{12}/gram butene-2 and which contained 63.2 weight percent trimethylpentanes.

Example 28

Amberlyst XN-1010 cation exchange resin/boron trifluoride catalyst was aged by continuously alkylating a 5/1 isobutane/butene-2 feed at $0°C$. and butene-2 WHSV of 2.5 grams/gram resin/hour with a continuous addition of 65 ppm of methanol.

During alkylation, the C_5-C_{12} yield declined from 1.86 to 1.25 grams C_5-C_{12}/gram of butene-2 and the trimethylpentane content of the C_5-C_{12} alkylate declined from 91 weight percent to 60 weight percent.

The aged resin catalyst was slurried in a methanol/alkylate solution. The source of this alkylate was the liquid product obtained from isobutane/butene-2 (cumulative ratio = 5.36 mole/mole) alkylation in a semi-batch reactor with Amberlyst XN-1010/BF$_3$ catalyst at $6°C$. and a WHSV of 2.4 grams olefin/gram resin/hour. The alkylate was obtained by weathering the reactor liquid at room temperature and atmospheric pressure. The methanol/alkylate/resin weight ratio was 5/1/1. The slurry was stirred for 4 hours at $60°C$., vacuum filtered to remove liquid (5 ml. methanol were used to facilitate transfer) and air dried on the vacuum filter for 5 minutes.

The resin so treated was tested for rejuvenation by carrying out a semi-batch reactor isobutane/butene-2 alkylation test at $0°C$. with an olefin WHSV of 2.4 grams butene-2/gram resin/hour and a cumulative isobutane/butene-2 ratio of 5.36 mole/mole. After 1 hour of reaction time under the above conditions, the treated resin produced a C_5-C_{12} alkylate with a yield of 2.1 grams C_5-C_{12}/gram butene-2 and which contained 62 weight percent trimethylpentanes.

Example 29

Amberlyst XN-1010 cation exchange resin/boron trifluoride catalyst was aged by continuously alkylating a 2/1 isobutane/butene-2 feed at 0°C. and butene-2 WHSV of 2.5 grams olefin/gram resin/hour for 30 hours at which point the C_5-C_{12} yield declined from 1.85 to 1.35 grams C_5-C_{12}/gram butene-2 converted and the trimethylpentane content of the C_5-C_{12} alkylate declined from 82 to 51 weight percent.

The liquid and gaseous contents of the reactor were drained, and isobutane and boron trifluoride were then charged to the reactor. As soon as the reactor attained a temperature of 0°C., 0.67 g water/g resin was injected directly into the reactor all at once, and 2/1 isobutane/butene-2 feed and boron trifluoride were fed continuously to the reactor as above. After 17 hours on stream, the C_5-C_{12} yield declined from 1.71 to 1.66 grams C_5-C_{12}/gram butene-2 converted and the trimethylpentane content of the C_5-C_{12} alkylate decreased from 67 to 53 weight percent.

The aged macroreticular resin was contacted with 500 ml. benzene in a Soxhlet apparatus for 4 hours. Excess benzene was removed by rinsing the resin with hexane followed by an extraction with hexane (500 ml) in a Soxhlet apparatus for 2 hours. Residual hexane was removed from the resin by drying it for about 16 hours at 120°C. at a total pressure less than 1 mm. Hg. The dried resin was then placed in a moist environment (air at 100 percent relative humidity) for 4.hours and dried for 3 hours at 120°C. under 25 in. Hg vacuum prior to use.

After processing a 5/1 isobutane/butene-2 feed for 3 hours at 0°C. and 2.5 olefin WHSV, the resin so treated was found to produce an alkylate with a C_5-C_{12} yield of only 0.3 gram C_5-C_{12}/gram butene-2 converted, thereby showing that use of benzene as a solvent did not afford the desired regeneration.

Example 30

Amberlyst-15 cation exchange resin/boron trifluoride catalyst was aged by continuously alkylating a 10/1 isobutane/butene-2 feed at 0°C. and butene-2 WHSV of 2.5 grams/gram resin/hour.

During alkylation, C_5-C_{12} yield declined from 1.88 to 1.35 grams C_5-C_{12}/gram of butene-2 converted and the trimethylpentane content of the C_5-C_{12} alkylate declined from 70 weight percent to 50 weight percent.

This aged catalyst was then regenerated four times using four different methods and after each regeneration the catalyst was tested for alkylation under the above conditions until the C_5-C_{12} yield declined to less than 1.0 grams C_5-C_{12}/gram of butene-2 converted.

In the fifth cycle of alkylation test the C_5-C_{12} yield declined from 1.86 to 0.82 grams C_5-C_{12}/gram of butene-2 converted and the trimethylpentane content of the C_5-C_{12} alkylate declined from 80 weight percent to 45 weight percent.

Regeneration of the aged catalyst from the fifth cycle of alkylation test was accomplished by slurrying it with acetone (acetone/resin = 27 grams/gram) for 4 hours at 40°C., removing the acetone regenerant by filtration followed by vacuum drying at 40°C. for 4 hours and then at room temperature for overnight.

The regenerated resin produced an alkylate with a C_5-C_{12} yield of 1.62 grams C_5-C_{12}/gram of butene-2 converted and a trimethylpentane content of 69 weight percent at 2 hours on stream under the above alkylation conditions.

Example 31

Amberlyst XN-1010/BF_3 catalyst was aged by continuously alkylating a 5/1 isobutane/butene-2 feed at 0°C. and 2.5 olefin WHSV until the yield declined to 0.7 gram C_5-C_{12}/gram C_4 olefin converted at which point the trimethylpentane content of the C_5-C_{12} alkylate was 53 weight percent. The liquid and gaseous materials were removed from the reactor and the resin was washed once with isobutane liquid. The isobutane was drained and then the resin was removed from the reactor.

A portion of the aged resin was subjected to water extraction in a Soxhlet apparatus for 4 hours and then dried for 3 hours at 120°C. under 25 in. Hg vacuum. This resin was tested for alkylation activity in a semi-batch reactor which contained isobutane, resin and BF_3. Butene-2 was added continuously to the reactor at an olefin WHSV of 2.26 for 3 hours. Analysis of the reactor liquid showed that alkylate was produced with a yield of 1.2 grams C_5-C_{12}/gram C_4 olefin converted and which contained 50.8 weight percent trimethylpentanes.

The enhanced results obtained utilizing a macroreticular resin/boron trifluoride catalyst regenerated by the method described herein are shown by the results set forth graphically in Figure 16. Referring to this figure, the C_5-C_{12} yield characteristics of fresh and regenerated resin are shown for isobutane/butene-2 alkylation using Amberlyst 15/boron trifluoride catalyst at 0°C. and 2.5 olefin WHSV. After 49 hours on stream, the C_5-C_{12} yield dropped from 1.85 to 1.35 grams C_5-C_{12} alkylate/gram C_4 olefin. The aged resin was then regenerated by the method described in Example 25. From the results shown, it is evident that equivalent yield performance was obtained by the regenerated resin up to about 20 hours on stream.

Figure 17 shows that the regeneration method described in Example 25 also restores the macroreticular resin in terms of product quality, i.e. the trimethylpentane content of the C_5-C_{12}

1,432,720

alkylate. After 50 hours on stream, the alkylate produced by reaction of isobutane and butene-2 using Amberlyst 15/boron trifluoride catalyst at 0°C. and 2.5 olefin WHSV contained only 50 weight percent trimethylpentanes. After regeneration, the alkylate produced by the resin after 10 hours on stream contained 76 weight percent trimethylpentanes, a quantity which was greater than that produced by the fresh resin at any time on stream.

The importance of the type of solvent used to perform the regeneration is illustrated by the results of Examples 27 and 29. In these examples, regeneration of the aged macroreticular resin was attempted using a paraffinic non-polar solvent, i.e. hexane and benzene respectively. As evident, no significant improvement in C_5-C_{12} yield was obtained.

The fact that the presence of alkylate during regeneration utilizing the polar solvent technique of the present invention does not destroy the effectiveness of such method to restore activity to the aged macroreticular resin is shown by the results of Example 28. In this example, the C_5-C_{12} yield was 1.25 grams/gram of butene-2 while after regeneration, such yield increased to 2.1 grams/gram of butene-2.

Experimental results showing the promotional effect hydrogen fluoride has on an inactive Amberlyst XN-1010/BF_3 catalyst for isobutane/butene-2 alkylation are shown in Table 5 below. These experiments were carried out in a 300 ml. stainless steel stirred autoclave under pressure using a semi-batch type operation. In accordance with a standard procedure 7 grams of the resin containing about 6 weight percent of water, 93 grams of isobutane and 1.8 grams of BF_3 when present, were initially placed in the reactor and 18 grams of butene-2 were subsequently continuously added over a period of one hour. Hydrogen fluoride, when present, was added to the reactor in an amount of 0.7 gram as a mixture with the isobutane. The course of the alkylation reaction was followed by means of an on-line gas chromatograph using a SCOT PAK column coated with squalane. Product analyses were performed similarly.

1,432,720

Table V

Example	32	33	34	35
Resin	Amberlyst XN-1010	Amberlyst XN-1010	Amberlyst XN-1010	Amberlite XAD-4
Water Content, wt.%	6	6	6	*
BF_3/H^+(Resin), eq./eq.	1.3	1.3	0	**
HF/H^+(Resin), eq./eq.	0	1.6	2.7	**
Cumulative $iC_4/C_4=$, mol/mol	5.4	5.2	5.3	4.9
Isobutane/Resin, g/g	13.3	12.8	13.2	13.3
Olefin WHSV, g olefin/g resin-hour	2.6	2.4	2.4	2.6
Temp. °C	2	3	0	1
RESULTS				
Olefin Conversion, %	8	93	trace	trace
Product Yield, gC_5^+/gC_4	0.9	1.37	—	—
Selectivity				
C_8 in C_5^+, wt.%	—	61	—	—
Trimethylpentanes in Octane Fraction, %	—	91	—	—
Alkylate Composition, mol %				
C_5	—	5.8	—	—
C_6	—	4.6	—	—
C_7	—	3.4	—	—
C_8	—	61.8	—	—
C_9	—	9.0	—	—
C_{10}^+	—	15.4	—	—

* Water added to reactor to give a resin water content of 8.6 wt.%.

** BF_3 and HF were added in an amount similar to that used in Example 2.
The molar ratio of BF_3/HF was 1.

From the above results, it will be seen that Example 32 shows that a catalyst comprised of Amberlyst XN-1010 cation exchange resin containing 6 weight percent water and boron trifluoride in an amount to provide 1.3 equivalents of boron trifluoride per equivalent of resin acid groups is not an effective alkylation catalyst as evidenced by the low olefin conversion and product yield. Example 33 shows that if HF is added in an amount equal to 1.6 equivalents of HF per equivalent of resin acid groups to the Amberlyst XN-1010/BF_3 catalyst whose composition is similar to that in Example 32, the new catalytic system is quite active for isoparaffin/olefin alkylation, as evidenced by the high degree of olefin conversion and the improved yield of alkylate. That HF in

combination with Amberlyst XN-1010 is not active for alkylation is clear from Example 34 from which it is seen that a catalyst comprised of Amberlyst XN-1010/HF failed to convert a significant amount of the olefin charged to the reaction zone.

The presence of acid groups in the resin is essential for alkylation activity. Such is shown by the results of Example 35. In this example, the levels of water, boron trifluoride and hydrogen fluoride in the reactor closely approximated those present in the system of Example 33, however, the resin employed in Example 35 contained no acidic groups. Without acid groups in the resin, no significant alkylation activity was observed.

WHAT WE CLAIM IS:-

1. A process for alkylating an isoparaffin having from 4 to 8 carbon atoms with an olefin having from 2 to 12 carbon atoms which comprises contacting the same in the liquid state at a temperature between −20°C. and 150°C. with a catalyst comprising a cation exchange resin containing acid groups and boron trifluoride, the molar ratio of said isoparaffin to said olefin being between 2 and 50, said resin being a macroreticular acid cation exchange resin having a water content between 0.5 and 20 weight percent and a surface acid concentration of less than 0.5 milliequivalents of hydrogen ion per square meter of surface area.

2. A process according to claim 1 wherein the boron trifluoride is present in an amount in excess of that needed to saturate the resin.

3. A process according to claim 1 in which the contacting is performed in the presence of 10 to 400 ppm. of water.

4. A process according to claim 1 or claim 3 wherein the resin contains a quantity of boron trifluoride between 0.1 eq. per equivalent of resin acid groups and the amount required for saturation of the resin, and also contains a quantity of hydrogen fluoride between 0.1 and 10 equivalents per equivalent of resin acid groups.

5. A process according to any of claims 1 to 4 wherein the resin is periodically regenerated by extraction with a polar solvent.

6. A process according to any preceding claim in which the boron trifluoride is added to a mixture of the isoparaffin and the resin, the resulting admixture is stirred to promote effective contacting of its components, and the olefin is added to the stirred admixture.

7. A process according to any of claims 1 to 5 in which the isoparaffin, olefin and boron trifluoride are continuously charged to the resin, the resulting admixture is continuously stirred to promote alkylation, and a hydrocarbon mixture containing alkylate is continuously withdrawn from said stirred admixture.

8. A process according to any preceding claim wherein said temperature is between −20°C. and 60°C.

9. A process according to any preceding claim wherein said surface acid concentration is between 0.001 and 0.2 milliequivalents of hydrogen ion per square meter of surface area.

10. A process according to any preceding claim wherein said resin is a macroreticular sulfonic acid cation exchange resin.

11. A process according to any of claims 1 to 3 and 5 to 10 wherein the equivalent ratio of BF_3 of resin acid groups exceeds 2.

12. A process according to any preceding claim wherein said olefin contains 4 carbon atoms.

13. A process according to any preceding claim wherein said isoparaffin is isobutane.

14. A process according to any preceding claim wherein said molar ratio of isoparaffin to olefin is between 3 and 10.

15. A process according to any preceding claim wherein said resin is a sulfonated styrenedivinylbenzene copolymer.

16. A process according to any of claims 10 to 15 wherein said macroreticular sulfonic acid cation exchange resin has a surface area of between 30 and 800 square meters per gram.

17. A process according to any of claims 3 to 16 wherein the amount of said water is 10 to 300 ppm.

18. A process according to any of claims 3 to 17 wherein the amount of said water is 20 to 200 ppm.

19. A process according to any of claims 3 to 18 wherein said water is employed in the form of a water-forming material.

20. A process according to claim 19 wherein said water-forming material is an alcohol.

21. A process according to claim 20 wherein said alcohol is methanol or tertiarybutyl alcohol.

22. A process according to any of claims 4 to 21 wherein said hydrogen fluoride is associated with said resin by virtue of having contacted the resin in admixture with the isoparaffin.

23. A process according to any of claims 5 to 22 wherein the polar solvent is water or an alcohol.

24. A process according to claim 23 wherein the alcohol has from 1 to 5 carbon atoms.

25. A process according to claim 24 wherein the alcohol is methanol.

For the Applicants,
CARPMAELS & RANSFORD,
Chartered Patent Agents,
43 Bloomsbury Square,
London WC1A 2RA.

Fig. I

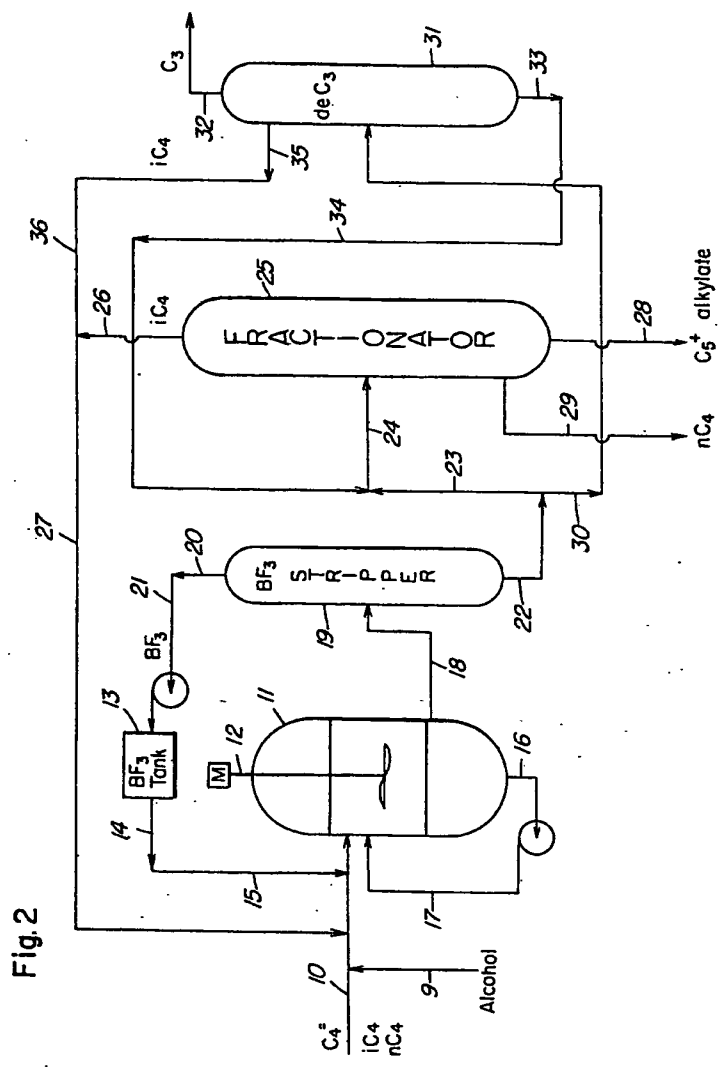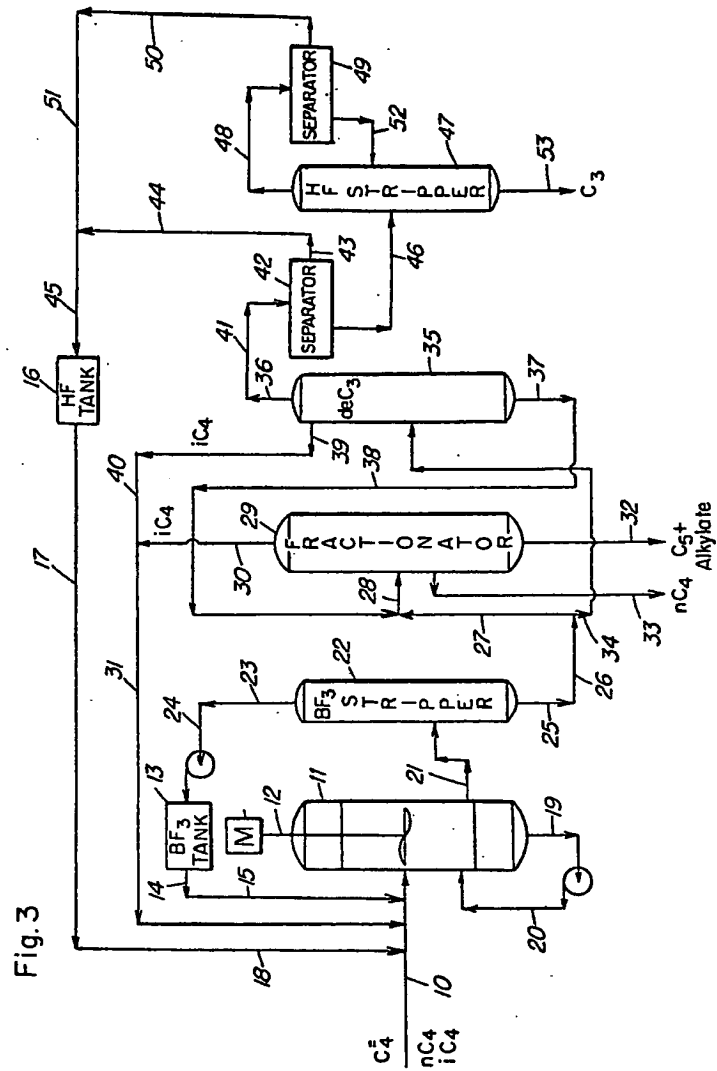Fig.2

Fig.3

Fig. 4

Fig.5

Fig.6

Semi-Continuous

Continuous

Yield, g C$_5$-C$_{12}$ Alkylate / g Olefin

Catalyst Age, g Olefin Charged / g Resin

Fig.7

Fig.8

Selectivity of TMP in C_5^+ and C_8 vs. Surface Area of Resin

Fig.9

RON Clear of C₅ Alkylate vs. Surface Area of Resin

Fig. 10

Fig. II
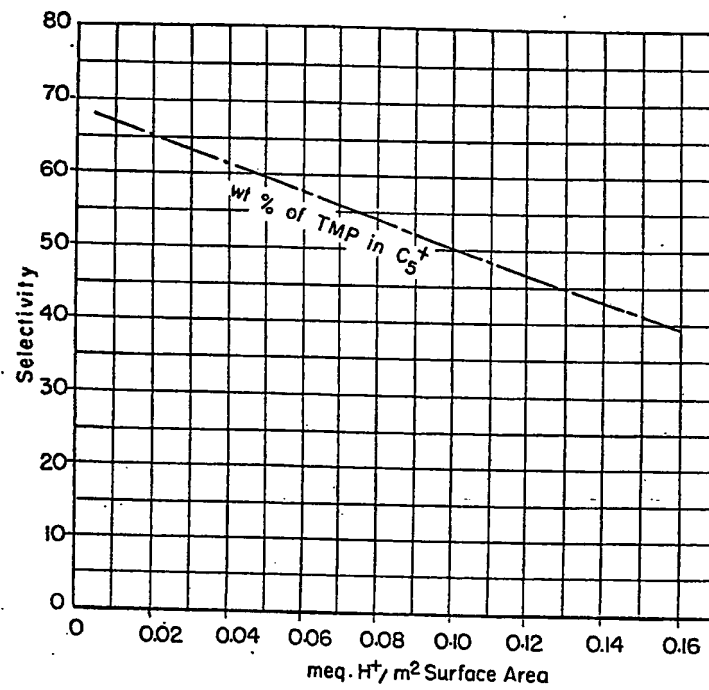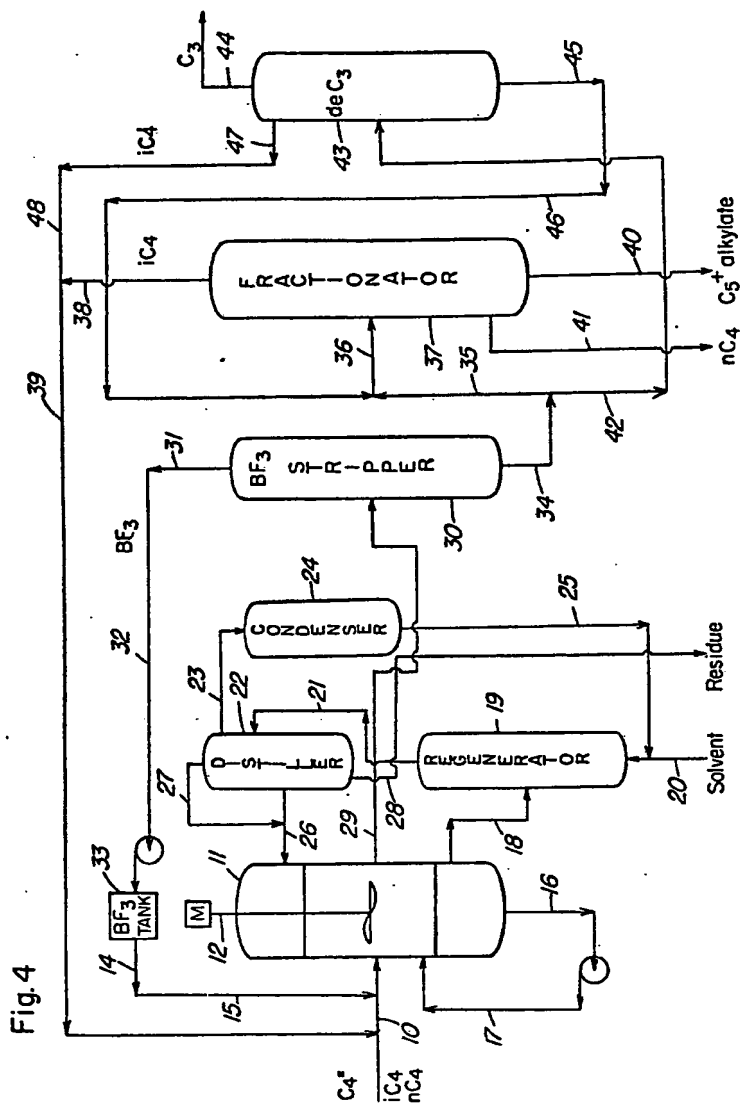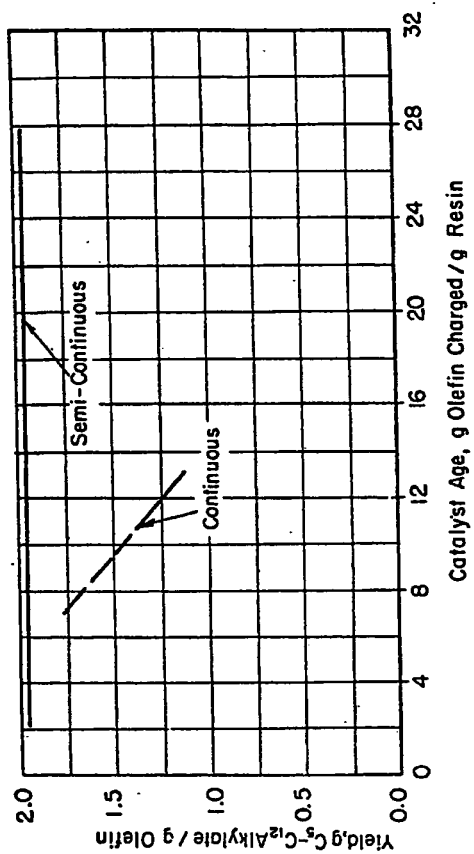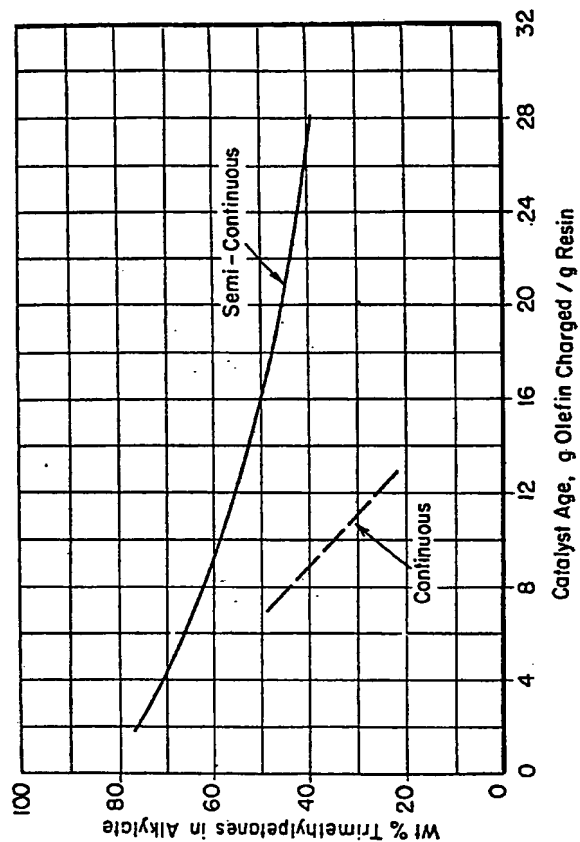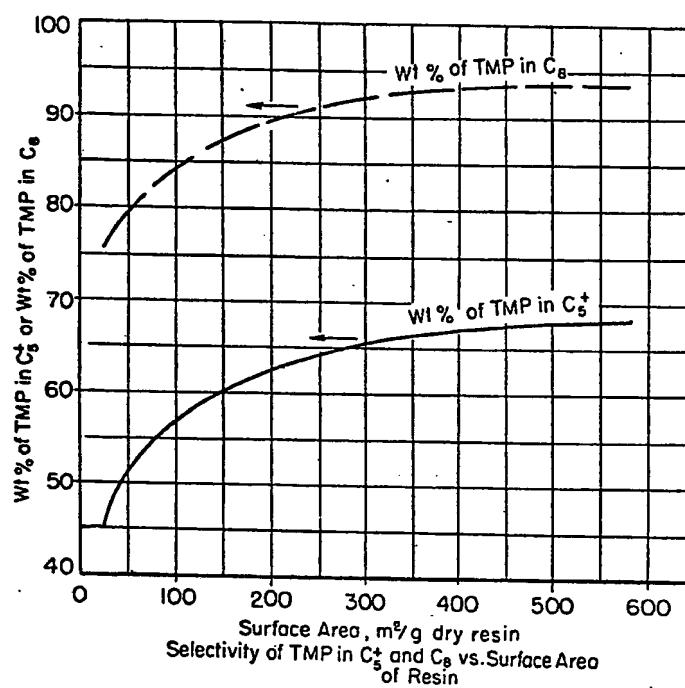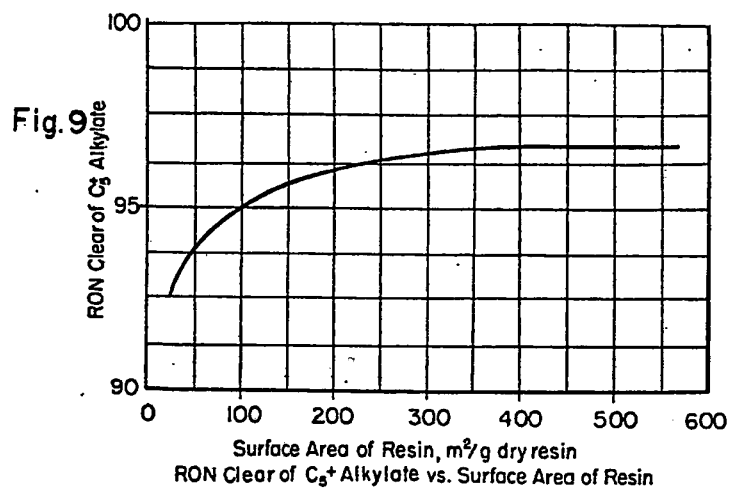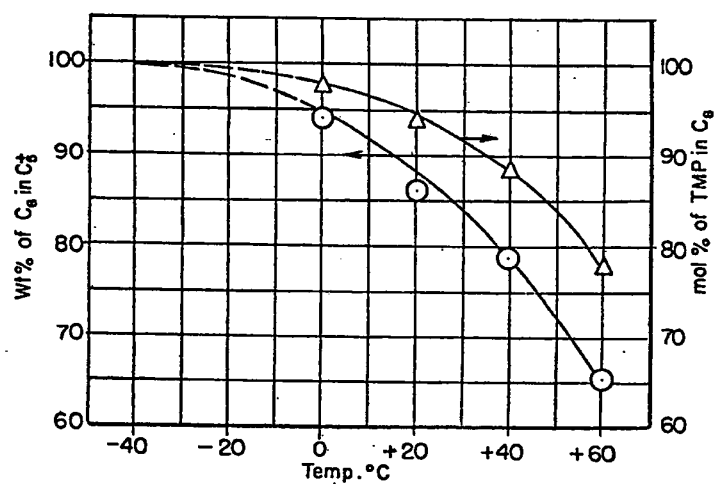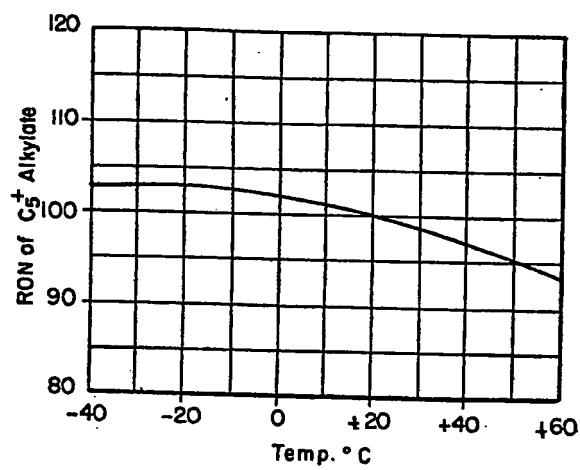
Fig.12
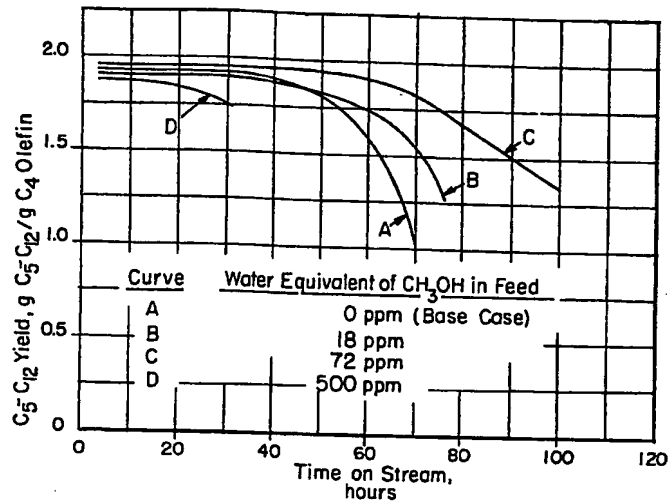
Fig. 13

Fig. 14

Fig. 15

Fig. 16

Fig. 17